ON A NEW CHEMICAL INDUSTRY ESTABLISHED BY M. CAMILLE VINCENT [1]

" A FTER I had made the discovery of the *marine acid air*, which the vapour of spirit of salt may properly enough be called, it occurred to me that, by a process similar to that by which this *acid* air is expelled from the spirit of salt, an *alkaline* air might be expelled from substances containing the volatile alkali. Accordingly I procured some volatile spirit of sal-ammoniac, and having put it into a thin phial and heated it with the flame of a candle, I presently found that a great quantity of vapour was discharged from it, and being received in a basin of quicksilver, it continued in the form of a transparent and permanent air, not at all condensed by cold."

These words, written by Joseph Priestley rather more than 100 years ago, describes the experiment by which ammonia was first obtained in the gaseous state. Unacquainted with the composition of this alkaline air, Priestley showed that it increased in volume when the electric sparks are passed through it, or when the alkaline air (ammonia) is heated, the residue consists of inflammable air (hydrogen). Berthollet, in 1788, proved that this increase in bulb is due to the decomposition of ammonia into nitrogen and hydrogen, whilst Henry and Davy ascertained that two volumes of ammonia are resolved into one volume of nitrogen and three volumes of hydrogen.

The early history of sal-ammoniac and of ammonia is very obscure. The salt appears to have been brought into Europe from Asia in the seventh century, derived, possibly, from volcanic sources. An artificial mode of producing the ammoniacal salts from decomposing animal matter was soon discovered, and the early alchemists were well acquainted with the carbonate under the name of *spiritus salis urinæ*. In later times sal-ammoniac was obtained from Egypt, where it was prepared by collecting the sublimate obtained by burning camel's dung.

Although we are constantly surrounded by an atmosphere of nitrogen, chemists have not yet succeeded in inducing this inert element to combine readily; so that we are still dependent for our supply of combined nitrogen, whether as nitric acid or ammonia, upon the decomposition of the nitrogenous constituents of the bodies of plants and animals. This may be effected either by natural decay giving rise to the ammonia, which is always contained in the atmosphere, or by the dry distillation of the same bodies, that is by heating them strongly out of contact with air, and it is from this source that the world derives the whole of its commercial ammonia and sal-ammoniac.

Coal—the remains of an ancient vegetable world—contains about 2 per cent. of nitrogen, the greater part of which is obtained in the form of ammonia when the coal undergoes the process of dry distillation. In round numbers 6,000,000 tons of coal are annually distilled for the manufacture of coal-gas in this country, and the ammoniacal water of the gas-works contains the salts of ammonia in solution.
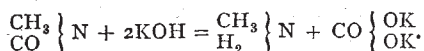
According to the most reliable data 100 tons of coal when distilled so as to yield 10,000 cubic feet of gas of specific gravity 0·6, give the following products, in tons :—

Gas.	Tar.	Ammonia Water.	Coke.	
22·25	8·5	9·5	59·75	Average.

This ammonia-water contains about 1·5 per cent. of ammonia; hence the total quantity of the volatile alkali obtainable from the gas-works in England amounts to some 9,000 tons per annum.
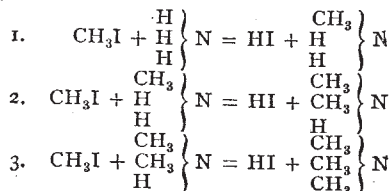
A singular difference is observed between the dry distillation of altered woody fibre as we have it in coal—and woody fibre itself. In the products of the first operation we chiefly find in the tar the aromatic hydrocarbons such as benzene, whilst in the second we find acetic acid and methyl-alcohol are predominant.

The year 1848 is a memorable one in the annals of revolutionary chemistry, for in that year Wurtz proved that ammonia is in reality only one member of a very large family. By acting with caustic potash on the nitriles of the alcohol radicals, he obtained the first series of the large class of compound ammonias, the primary monamines. Of these, methylamine is the first on our list :—

$$\left.\begin{array}{c}CH_3 \\ CO\end{array}\right\}N + 2KOH = \left.\begin{array}{c}CH_3 \\ H_2\end{array}\right\}N + CO\left\{\begin{array}{c}OK \\ OK.\end{array}\right.$$

The years that followed, 1849-51, were prolific in ammoniacal discovery. Hofmann pointed out that not only one atom of hydrogen in ammonia can be replaced by its equivalent of

organic radical, but that either two or all of the three atoms of the hydrogen in ammonia can be likewise replaced, giving rise to the secondary and tertiary amines by the following simple reactions :—

$$1. \quad CH_3I + \left.\begin{array}{c}\cdot H \\ H \\ H\end{array}\right\}N = HI + \left.\begin{array}{c}CH_3 \\ H \\ H\end{array}\right\}N$$

$$2. \quad CH_3I + \left.\begin{array}{c}CH_3 \\ H \\ H\end{array}\right\}N = HI + \left.\begin{array}{c}CH_3 \\ CH_3 \\ H\end{array}\right\}N$$

$$3. \quad CH_3I + \left.\begin{array}{c}CH_3 \\ CH_3 \\ H\end{array}\right\}N = HI + \left.\begin{array}{c}CH_3 \\ CH_3 \\ CH_3\end{array}\right\}N$$

To these bodies the names of methylamine, dimethylamine, and trimethylamine were respectively given. They resemble ammonia in being volatile alkaline liquids or gases, which combine with acids to form crystallisable and well defined salts.

Hitherto, these compound ammonias have been chemical curiosities; they have, however, recently become—as has so often been the case in other instances—of great commercial importance, and are now manufactured on a large scale.

We are all well aware that the French beet-root sugar industry is one of great magnitude, and that it has been largely extended in late years. In this industry, as in the manufacture of cane-sugar, large quantities of molasses or treacle remain behind after the whole of the crystallisable sugar has been withdrawn. These molasses are invariably employed to yield alcohol by fermentation. The juice of the beet, as well as that of the sugar-cane, contains, in addition to the sugar, a large quantity of extractive and nitrogenous matters, together with considerable quantities of alkaline salts. In our sugar-producing colonies, the waste liquors or spent-wash from the still—called *vinasses* in French—are wastefully and ignorantly thrown away instead of being returned to the land as a fertiliser, and thus the soil becomes impoverished.

In France it has long been the custom of the distiller to evaporate these liquors (*vinasses*) to dryness, and calcine the mass in a reverbatory furnace, thus destroying the whole of the organic matter but recovering the alkaline salts of the beet-root. In this way 2,000 tons of carbonate of potash are annually produced in the French distilleries. More than thirty years ago the idea was entertained of collecting the ammonia-water, tar, and oils which are given off when this organic matter is calcined, but the practical realisation of this project has only quite recently been accomplished, and a most unexpected new field of chemical industry thus opened out through the persevering and sagacious labours of M. Camille Vincent, of Paris.

The following is an outline of the process as carried out at the large distillery of Messrs. Tilloy, Delaune, and Co., at Courrières. The spent-wash, having been evaporated until it has attained a specific gravity of 1·81, is allowed to run into cast-iron retorts, in which it is submitted to dry distillation. This process lasts four hours, the volatile products pass over, whilst a residue of porous charcoal and alkaline salts is left behind in the retort. The gaseous products given off during the distillation are passed through coolers, in order to condense all the portions which are liquid or solid at the ordinary temperature, and the combustible gases pass on uncondensed, and to serve as fuel for heating the retorts.

The liquid portion of the distillate is a very complex mixture of chemical compounds resembling, in this respect, the corresponding product in the manufacture of coal-gas. Like this latter, the liquid distillate from the spent-wash may be divided into—1. The ammonia water; 2. The tar. The ammonia water of the vinasses resembles that of the coal-gas manufacture, in so far as it contains the carbonate, sulphydrate, and hydrocyanide of ammonia; but it differs from this (and approximates to the products of the dry distillation of wood) by containing, in addition, methyl alcohol, methyl sulphide, methyl cyanide, many of the members of the fatty acid series, and, most remarkable of all, *large quantities of the salts of trimethylamine.*

The tar, on redistillation, yields more ammonia water, a large number of oils, the alkaloids of the pyridene series, solid hydrocarbons, carbolic acid, and lastly, a pitch of fine quality.

The crude alkaline aqueous distillate is first neutralised by sulphuric acid, and the saline solution evaporated, when crystals of sulphate of ammonia are deposited, and these, after separating and draining off, leave a mother-liquor, which contains the more soluble sulphate of trimethylamine. During the process of

concentration, vapours of methyl alcohol, methyl cyanide and other nitriles, are given off, these are condensed and the cyanide used for the preparation of ammonia and acetic acid by decomposing it with an alkali.

Trimethylamine itself is at present of no commercial value, though we are not without hopes that a useful employment for this substance may soon be found. The question arises as to how this material can be made to yield substances capable of ready application in the arts. This problem has been solved by M. Vincent in a most ingenious way. He finds that the hydrochlorate of trimethylamine, when heated to a temperature of 260°, decomposes into (1) ammonia, (2) free trimethylamine, and (3) chloride of methyl :—

$$3NMe_3HCl = 2NMe_3 + NH_3 + 3MeCl.$$

By bubbling the vapours through hydrochloric acid, the alka-
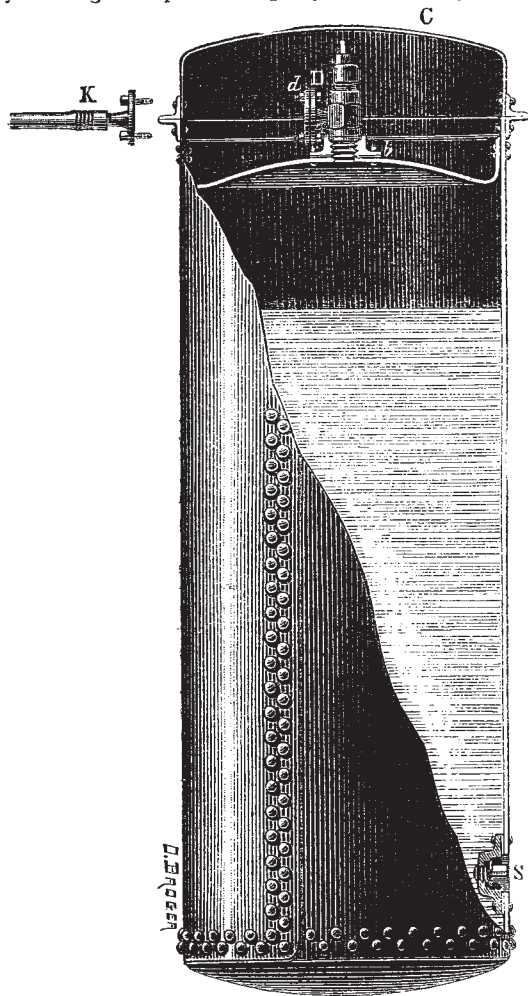

FIG. 1.

line gases are retained, and the gaseous chloride of methyl passes on to be purified by washing with dilute caustic soda and drying with strong sulphuric acid. This is then collected in a gas-holder, whence it is pumped into strong receivers and liquefied. The construction of one of these is shown in Fig. 1. They consist of strong wrought-iron cylinders, tested to resist a pressure of 20 kilos per square centimeter, and containing 50, 110, or 220 kilos of chloride of methyl. The liquid is drawn from these receivers by opening the screw tap (D), which is covered by a cap (C) to prevent injury during transit.

Both ammonia and chloride of methyl are, however, substances possessing a considerable commercial value. The latter compound has up to this time, indeed, not been obtained in large quantities, but it can be employed for two distinct purposes —1. It serves as a means of producing artificial cold. 2. It is

most valuable for preparing certain methylated dyes, which are at present costly, inasmuch as they have hitherto been obtained by the use of methyl iodide, an expensive substance.

Methyl chloride was discovered in 1840 by MM. Dumas and Peligot, who obtained it by heating a mixture of common salt, methyl alcohol, and sulphuric acid. It is a gas at the ordinary temperature, possesses an ethereal smell and a sweet taste, and its specific gravity is 1·738. It is somewhat soluble in water (about 3 volumes), but much more in acetic acid (40 volumes), and in alcohol (35 volumes). It burns with a luminous flame tinged at the edges with green, yielding carbonic and hydrochloric acids. Under pressure, methyl chloride can readily be condensed to a colourless, very mobile liquid, boiling at − 23 C. under a pressure of 760 mm. As the tension of the vapour is not high, and as it does not increase very rapidly with the temperature, the liquefaction can be readily effected, and the collection and transport of the liquefied chloride can be carried on without danger. The following table shows the tension of chloride of methyl at varying temperatures :—

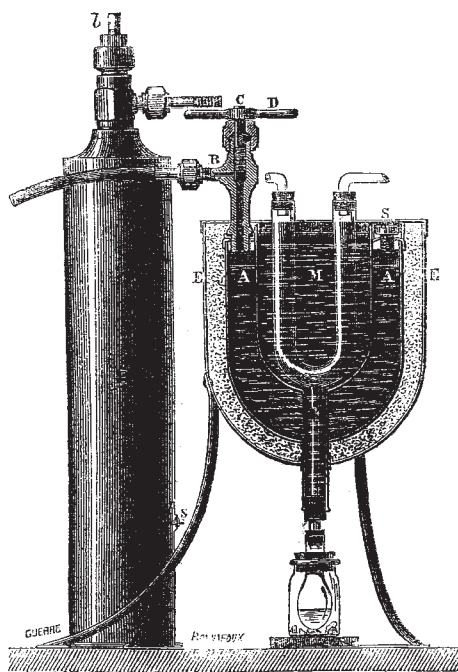| At 0°	the tension of CH_3Cl is 2·48 atmospheres.
,, 15°	,, ,, 4·11 ,,
,, 20°	,, ,, 4·81 ,,
,, 25°	,, ,, 5·62 ,,
,, 30°	,, ,, 6·50 ,,
,, 35°	,, ,, 7·50 ,,

FIG. 2.

From these numbers we must of course subtract 1 to obtain the pressure which the vapour exerts upon the containing vessel.

As a means of producing low temperatures chloride of methyl will prove of great service both in the laboratory and on a larger industrial scale. When the liquid is allowed to escape from the receiver into an open vessel, it begins to boil, and in a few moments the temperature of the liquid is lowered by the ebullition below − 23°, the boiling-point of the chloride. The liquid then remains for a length of time in a quiescent state, and may be used as a freezing agent. By increasing the rapidity of the evaporation by means of a current of air blown through the liquid, or better, by placing the liquid in connection with a good air-pump, the temperature of the liquid can in a few minutes be reduced to − 55°, and large masses of mercury easily solidified.

The construction of a small copper receiver and of the freezing-machine employed by M. Camille Vincent is shown in Fig. 2. It consists of a double-cased copper vessel, between the two sides of which the methyl-chloride is introduced. The central space is filled with some liquid such as alcohol, incapable of solidification. The chloride of methyl is allowed to enter by the screw-tap (B), and

the screw (s) left open to permit of the escape of the gas. As soon as the whole mass of liquid has been reduced to a temperature of − 23° the ebullition ceases, the screw (s) may be replaced, and if a temperature lower than − 23° be required the tube (B) placed in connection with a good air-pump. By this simple means a litre of alcohol can be kept for several hours at temperatures either of − 23° or − 55°, and thus a large number of experiments can be performed for which hitherto the expensive liquid nitrous oxide or solid carbonic acid was required.

M. Camille Vincent has recently constructed a much larger and more perfect and continuous form of freezing-machine, in which, by means of an air-pump and a forcing-pump, the chloride of methyl is evaporated in the freezing-machine, and again condensed in the cylinders. This enlarged form of apparatus will probably compete favourably with the ether- and sulphurous acid freezing-machines now in use, as they can be simply constructed, and as the vapour and liquid employed does not attack metal, is non-poisonous, and as the frigorific effects which it is capable of producing are most energetic.

The second and perhaps more important application of methyl-chloride is to the manufacture of methylated colours.

It is well known that rosaniline or aniline red, $C_{20}H_{19}N_3$, yields compounds possessing a fine blue violet or green colour, when a portion of the hydrogen has been replaced by the radicals, methyl or ethyl, and the larger the proportion of hydrogen replaced, the deeper is the shade of violet produced. Then we have triethyl rosaniline, or Hofmann's[1] violet, $C_{20}H_{16}(C_2H_5)_3N_3$.

By the replacing one or two atoms of the hydrogen of aniline by methyl, and by oxidising the methyl-aniline, Charles Lauth obtained fine violet colours, whilst about the same time Hofmann observed the production of a bright green colouring matter now known as iodine green, formed during the manufacture of the violet, and produced from this latter colour by the action of methyl-iodide.

In order to prepare aniline green from the pure chloride of methyl a solution of methyl-aniline violet in methyl-alcohol is placed in an iron digester, and the liquid rendered alkaline by caustic soda. Having closed the digester, a given quantity of liquid chloride of methyl is added by opening a tap, and the digester thus charged is placed in a water bath, heated by a jet of steam until the temperature reaches 95°, and the indicated pressure amounts to from 4 to 5 atmospheres. As soon as the reaction is complete the hot water is replaced by cold, and the internal pressure reduced by opening the screw-tap of the digester. The product of this reaction, heated and filtered, yields the soluble and colourless base, whose salts are green. To the acidified solution a zinc-salt is added to form a double salt, and the green compound is then precipitated by the addition of common salt. By adding ammonia to a solution of the methyl green salt, a colourless liquid is obtained in which cloth mordanted with tannic acid and tartar-emetic becomes dyed green (R. S. Dale).

If rosaniline be substited for methyl-aniline in the preceding reaction, Hofmann's violet is obtained. The application of methyl-chloride to the preparation of violets and greens is, however, it must be remembered, not due to M. Vincent; it has been practised for some years by various aniline colour makers. M. Vincent's merit is in establishing a cheap method by which perfectly pure chloride of methyl can be obtained, and thus rendering the processes of the manufacture of colours much more certain than it has hitherto been. By the use of this material the aniline can be methylated in simple cast-iron boilers heated by steam, and under a pressure much more moderate than is otherwise required.

In reviewing the new chemical industry of the beet-root vinasses one cannot help being struck by the knowledge and ability which have been so successfully expended by M. Camille Vincent, on the working out of the processes. Here again we have another instance of the utilisation of waste chemical products and of the preparation on a gigantic scale of compounds hitherto known only as chemical rarities. All those interested in the progress of scientific research must congratulate M. Camille Vincent on this most successful issue of his labours.

ILLUMINATION IN SPECTROSCOPY[2]

AFTER having shown how intrinsic brilliancy of the light operated on was the chief visual step to excellence in spectroscopic observations, the author proved that the temperature

[1] Hofmann, *Proc.* Roy. Soc., xiii. 13 (1863).
[2] Abstract of paper upon "End-on, in Place of Transverse, Illumination in Private Spectroscopy," by Mr. Piazzi Smyth, Past President of R. Sc. Soc. Arts. Edinb., February 10, 1879.

of the light must be kept constant, or we might be landed in a totally different class of physical phenomena of a most confounding character.

Coming, then, practically to *flame*-spectroscopy, he described the results hitherto obtained by all the leading spectroscopists respecting the peculiar lines and bands, all of them very faint, of the blue-grey blowpipe flame of coal-gas and common air ; and then showed how, by merely looking at one and the same flame *end-on*, in place of transversely, according to the usual custom, all the features hitherto chronicled may be seen some five times brighter ; while many other details not dreamt of before come into view, and the temperature remains undisturbed.

Next applying the same principle to the electric-spark illumination of gas-vacuum tubes, a still greater proportional improvement was obtained. But not until the author had invented or arranged a new description of such tubes, which rendered the application of the end-on principle possible. Examples of these new tubes, as prepared lately for the author by M. Salleron, 24, rue Pavée au Marais, Paris, were exhibited ; and several proofs of their superior brightness of illumination were given. The last being that in a narrow and critical region of a rather faint and difficult carbonaceous spectrum, where the Royal Society, London, has published eight lines only, and those dark ones—the new tubes showed thirty-one lines, and all of them bright ones. As yet the author had only been able to get twelve different gases thus prepared ; but with such decided improvement of spectroscopic vision in every case, that he hopes so increased a demand may soon flow in upon M. Salleron, as will make it worth his while to prepare similar end-on tubes of all known volatile products ; and the result can hardly but prove most favourable to the progress of spectroscopic science.[1]

UNIVERSITY AND EDUCATIONAL INTELLIGENCE

DR. J. H. BALFOUR, Professor of Botany in the Edinburgh University, has resigned his chair, which he has filled since 1845, on account of failing health. The patronage of the Chair of Botany is vested in the curators of the University. Among the candidates for the chair, we learn, are Mr. Carruthers, Prof. Dickson, of Glasgow, Mr. J. Bailey Balfour, and Prof. McNab, of Dublin.

THERE was much fine talk last Wednesday at the Mansion House on the subject of University extension in London, and it was pleasing to see a prince take an apparently genuine interest in the intellectual advancement of the people. We sincerely hope that the movement may lead to a substantial and durable result, though we very much doubt it. What we want most in London is a true university after the German model, not a "Cambridge extension." We are glad that Prince Leopold, in his really able address at the Birkbeck Institution on Tuesday, insisted so strongly on the weak point of the British workman, and that he can only hope to hold his own by the side of the foreign workman by starting with an equally good education.

AT the annual meeting of the trustees of the Birmingham Science College, under the presidency of the founder, Sir Josiah Mason, who celebrated on Monday his eighty-fourth birthday, it was announced that the college building, a handsome Gothic structure in the rear of the Birmingham Town Hall, is rapidly approaching completion, and the formal opening will probably be made on the founder's next birthday. Nearly 150,000*l*. has been expended on the college building and endowment.

SCIENTIFIC SERIALS

American Journal of Science and Arts, February.—We have here two interesting papers on acoustics. Mr. Jacques has inquired into the velocity of loud sounds, measuring the velocity at different short distances from a cannon by means of a series of membranes electrically connected with a chronograph. He finds that the velocity of sound is a function of its intensity, and that experiments in which a cannon is used contain an error, probably due to the bodily motion of the air near the cannon. Immediately in the rear of the cannon the velocity was less than at a distance, but, going from the cannon, the velocity rose to a maximum considerably above the ordinary velocity, and then fell gradually to the rate usually received. When the cannon was pointed

[1] Tubes similar to those referred to are already well-known in England; Dr. Monckhoven has in fact pointed out the value of such tubes, and sent specimens to several observers in England.—ED.